

**VANADIUM K XANES STUDIES OF EET79001 IMPACT-MELT GLASSES REVISITED.** S. R. Sutton<sup>1,2</sup>, M. N. Rao<sup>3</sup>, L. E. Nyquist<sup>4</sup> and D. K. Ross<sup>5,6</sup> <sup>1</sup>Dept. of Geophysical Sciences and <sup>2</sup>CARS, University of Chicago, Chicago, IL 60439, <sup>3</sup>SCI, Johnson Space Center, Houston, TX 77058, <sup>4</sup>XI/NASA Johnson Space Center, Houston, TX 77058, <sup>5</sup>Jacob JETS, NASA Johnson Space Center, Houston, TX 77058, <sup>6</sup>UTEP-CASSMAR.

**Introduction:** Some impact-melt glasses in shergottites are rich in Martian atmospheric noble gases and sulfur suggesting a possible association with regolith-derived secondary mineral assemblages in the shocked samples. Previously, we studied two glasses, # 506 (Lith C in Lith A) and # 507 (Lith C in Lith B) from EET79001 [1,2] and suggested that sulfur initially existed as sulfate in the glass precursor materials and, on shock-melting of the precursors, the sulfate was reduced to sulfides in the shock glasses.

To examine the validity of this hypothesis, we used V K microXANES techniques to measure the valence states of vanadium in the Lith C glasses from Lith A and Lith B in EET79001 [3] to complement and compare with previous analogous measurements on ,78 glass (Lith C in Lith A) [4,5]. We reported the preliminary results in [3]. Vanadium is ideal for addressing the redox issue because it has multiple valence states and is a well-studied element. Vanadium in basalts exists mostly as  $V^{3+}$ ,  $V^{4+}$  and  $V^{5+}$  in terrestrial samples, mainly as  $V^{3+}$  with minor  $V^{2+}$  and minor  $V^{4+}$  in lunar samples and as roughly equal mixtures of  $V^{3+}$  and  $V^{4+}$  in Martian meteorites [6].

In this report, we discuss the application of the V K XANES results to decipher the nature of shock reduction occurring in the silicate glasses during the impact process.

**Results:** We briefly recall the previous findings. The vanadium valence measurements for impact glass ,78 (Lith C in Lith A) in EET79001 [4,5] at three different locations earlier yielded valence values of 3.1, 3.2 and 3.4 with inferred  $fO_2$  values of IW-0.7, IW-0.1 and IW+0.7, respectively. This range of oxygen-fugacity values is understandable because these glasses are shock-molten impact products which are heterogeneous in composition. Oxygen fugacity values obtained from the analysis of Fe-Ti oxides [7] and Eu partitioning in pyroxenes [8] from EET79001 Lith A and Lith B (host lithologies) were IW+0.3 to IW+2 suggesting that V in #78 might have been reduced during the impact process [4,5].

We analyzed two regions in the Y-shaped glass vein in the 506 (Lith C in Lith A) (Fig.1). At the first region, a line scan was carried out collecting XANES spectra in 4 micron steps across the vein. The V valences obtained range from 3.03 to 3.09 with a mean value of  $3.06 \pm 0.03$  which closely resembles that of the pure  $V^{3+}$  species. These results yield  $fO_2$  values between IW-0.8 and IW-1.1 with a mean of IW-0.9  $\pm$

0.1, assuming equilibrium at a liquidus temperature of 1400 °C [4]. At the second region, three more analyses were performed at the center and two edges of the Y-shaped vein in Fig.1. Here, the vanadium valence ranged from 2.86 to 2.96 with a mean value of  $2.91 \pm 0.05$  with the inferred  $fO_2$  corresponding to values between IW-1.4 and IW-2.0 with a mean of IW-1.7  $\pm$  0.1. These results indicate that region 2 is more reduced than region 1. Combining the data for the two regions yields a mean value of  $3.01 \pm 0.03$  and a mean  $fO_2$  value of IW-1.2  $\pm$  0.01. These results indicate that the glassy regions in #506 are dominated by  $V^{3+}$  with perhaps small amounts of  $V^{2+}$  in some locations.

Further, in the #507 glass (Lith C in Lith B), three regions were analyzed for V K XANES (Fig. 2). Two regions which contain sulfur-rich blebs nearby yielded vanadium valences of 3.6 and 3.8 while the “bleb-free” region gave a valence of 3.4. The mean V valence of the three spots was  $3.59 \pm 0.06$  yielding a mean  $fO_2$  of IW+1.4  $\pm$  0.2. All the three regions contained mixtures of  $V^{3+}$  and  $V^{4+}$ . The bleb-rich region (V valence  $3.76 \pm 0.10$  corresponding to the  $fO_2$  value of IW+2.1  $\pm$  0.3) indicates relatively higher proportion of  $V^{4+}$  than the bleb-free region (V valence of  $3.43 \pm 0.1$  corresponding to  $fO_2$  value of IW+0.8  $\pm$  0.3). These results show that #507 glass contains more oxidized V than #506 glass.

**Discussion:** Compared to the previously reported Lith C glass V results (mean V valence of 3.2 corresponding to a mean  $fO_2$  value of IW) obtained by [4, 5], it appears that the 506 glass (Lith A) is about one log unit more reduced (i.e.,  $V^{3+}$  dominated). Note that 507 glass (Lith B) is about one log unit more oxidized relative to 506 and 78 containing material with mixtures of  $V^{3+}$  and  $V^{4+}$ . These results suggest that the #507 Lith B glass  $fO_2$  inferred from V valence falls in the range of  $fO_2$  values obtained from Fe-Ti oxide [6] whereas the inferred 506 Lith A glass  $fO_2$  is relatively more reduced. This reduction presumably occurred during shock heating/cooling of the silicate glass precursors due to isentropic cooling [9]. Note that #506 and #78 belong to the olivine phyric group whereas #507 glass belongs to the pyroxene phyric group of shergottites.

What is the oxidation state of parent vanadium in the host rock Lith A and Lith B in EET79001 prior to shock melting? [8] observed that pigeonite is one of the first minerals to crystallize from a shergottite melt, whereas Fe-Ti oxides arrive on the liquidus late in the crystallization sequence [10]. Based on their Eu anal-

yses, [8] deduced  $fO_2$  values of  $IW+1.1 \pm 0.2$  for Lith A and  $IW+0.3 \pm 0.1$  for Lith B in EET79001 which are somewhat more reduced than the corresponding values estimated by [7] using Fe-Ti oxides. In this context, [11] determined a  $fO_2$  value of  $IW+0.9$  for Y980459 (an olivine phyric shergottite similar to Lith A) using techniques based on vanadium partitioning in olivine/melt. Moreover, as our 506 sample is more strongly reduced compared to others during the impact shock process as shown in Fig. 1 of [3], it shows reduction during isentropic cooling [9] in the impact glass yields a lower value for the mixed V valence, perhaps producing  $V^{2+}$ .

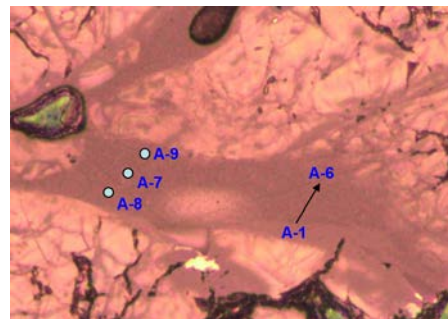
The  $fO_2$  value of  $IW+1.1$  determined for Lith A by [8] suggests that vanadium in Lith A is a mixture of  $V^{3+}$  and  $V^{4+}$  with  $V^{3+}$  being dominant. Using this valence estimate for the host precursor, the vanadium results obtained by us for 506 glass consisting of mostly shock-molten Lith A host correspond to a more reduced  $fO_2$  value of  $IW-1.2$ , demonstrating that  $V^{3+}$  is dominant in the glass and is partly reduced to  $V^{2+}$  during isentropic cooling of shock melt.

Based on the Eu results, [8] derived a  $fO_2$  value of  $IW+0.3$  for Lith B. In contrast, we find a high mean V valence value of 3.6 in # 507. Moreover, there is a significant difference in the mixed V valence between the bleb-rich and bleb-free regions: the bleb-rich region yields a V valence of  $3.76 \pm 0.10$  whereas the bleb-free region yields a V valence value of  $3.43 \pm 0.10$  corresponding to  $fO_2$  values of  $IW+2.1 \pm 0.3$  and  $IW+1.4 \pm 0.3$  respectively.

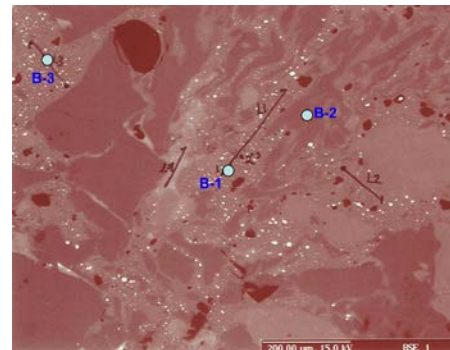
The previous V valence results reported in [3] were based on the intensity of the pre-edge peak using the protocol of [4]. This method provides an “effective” or “average” valence. A result of 3.5 can be produced by various mixtures of the 4 possible valence states of vanadium. This method however does not allow identification of the individual mixed species. The assumption here is that a result of 3.5 is produced by equal mixtures of  $V^{3+}$  and  $V^{4+}$  since redox buffers generally involve species of adjacent charge state. But, these mixed species can be identified by performing linear combination fittings of the full spectra using the full spectra for standards. Recently, we have revisited and carried out this linear combination fitting on the 507 glass spectra. Using the pre-edge method, the three different spots gave valences of 3.57, 3.43, and 3.76 with uncertainties of  $\sim 0.1$  ( $1\sigma$ ) for a mean of  $3.59 \pm 0.06$ . For the linear combination fitting, we merged these three spectra into a single spectrum to improve the signal-to-noise ratio (justified since the valences are similar) and used spectra for three Schreiber glasses (FAD) for standards ( $X_{112}=3.12$ ,  $X_{110} = 3.69$ ,  $X_{116}=4.84$ ; dominated by  $V^{3+}$ ,  $V^{4+}$  and  $V^{5+}$ , respectively). The fitting results were  $X_{112}=76 \pm 4 \%$ ,  $X_{110}$

$= 26 \pm 4 \%$ , and  $X_{116} = 0 \pm 1 \%$  leading to an effective valence of 3.62 which agrees well with the mean pre-edge result of 3.59. The full spectrum fitting supports the view that the vanadium currently in the 507 glass is a mixture of  $V^{3+}$  and  $V^{4+}$  with no more than a few percent of  $V^{5+}$  (if any).

**Conclusions:** Vanadium K XANES results for EET79001 impact glasses discussed here show that in #507 glass, roughly equal proportions of  $V^{3+}$  and  $V^{4+}$  remain whereas in #506 and #78 glasses, vanadium has been reduced to predominantly  $V^{3+}$  with possible minor  $V^{2+}$  during isentropic cooling of the shock melt [8]. The extent of shock reduction of V varies from one site to another in these glasses suggesting that part of the parent V may have escaped significant reduction during the shock process, especially in 507 where V is still relatively oxidized.



**Fig. 1:** Regions in # 506 scanned for V K XANES.



**Fig. 2:** Bleb-free and bleb-rich regions in #507 glass scanned for V K XANES.

**References:** [1] Rao M. N. et al. (2004) *LPS XXXV*, #1501. [2] Sutton S. R. et al. (2008) *LPS XXXIX*, #1961. [3] Sutton S. R. et al. (2010), *LPS XXXXI*, #1747. [4] Sutton S. R. et al. (2005) *GCA* 69, 2333-2348. [5] Karner J. M. et al. (2006) *Am. Min.* 91, 270-277. [6] Papike J. J. et al. (2005) *Am. Mineral.* 90, 277-290. [7] Herd C. D. K. et al. (2001) *Am. Min.* 86, 1015-1024. [8] McCanta M.C. et al. (2004) *GCA*, 68, 1943 - 1952. [9] Sheffer A. and Melosh H. J. (2005) *LPS XXXVI*, #1468. [10] Minitti M. and Rutherford (2000) *GCA*, 64, 2535-2547 [11] Shearer C. K. et al. (2006) *Am. Mineral.* 91, 1657 -1663.